

indanol have been described, and several derivatives of these alcohols have been made.

It has been demonstrated that  $\alpha$ -indanol exists in two distinct polymorphs.

This alcohol condenses readily with itself and

with ethyl alcohol to yield indanyl ethers.

Two isomeric forms of diindanyl ether have been separated, one melting at 68° and the other at 74°.

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RECEIVED OCTOBER 15, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## Reactions of Perinaphthene Derivatives

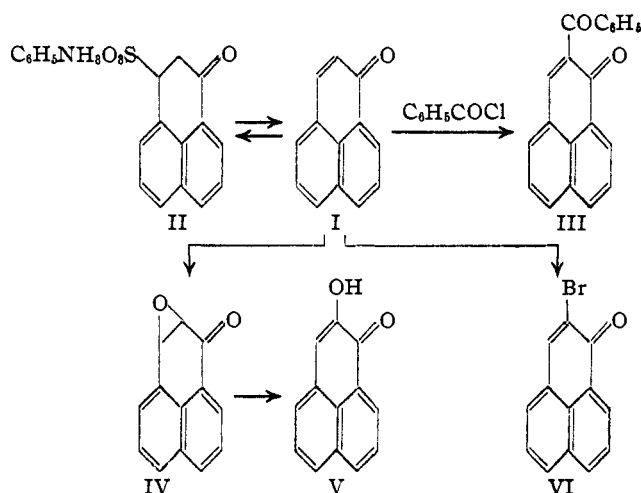
BY LOUIS F. FIESER AND LAWRENCE W. NEWTON

Interest in the utilization of perinaphthenone and perinaphthanone derivatives as starting materials for the synthesis of polynuclear aromatic compounds<sup>1</sup> prompted the present exploratory study of other reactions of available members of the series.

Perinaphthenone (I), which is obtainable in quantity from  $\beta$ -naphthol and glycerol,<sup>2,1a</sup> resembles benzanthrone, of which it may be considered the parent substance, in giving a red vat with alcoholic alkali and hydrosulfite. Like an unsubstituted quinone, the bright yellow  $\alpha,\beta$ -unsaturated ketone reacts with sodium bisulfite to give a colorless addition product, which was isolated in the form of an aniline salt presumably having the structure II; treatment of the salt with dilute hydrochloric acid at the boiling point results in the reversal of the reaction and precipitation of the ketone I. Although Zil'berman and Barkov<sup>3</sup> state that perinaphthenone reacts with hydroxylamine to give a nitrogen-free product, we found that the expected oxime can be obtained by refluxing the ketone with hydroxylamine hydrochloride in alcohol. Attempts to utilize perinaphthenone as a component in the Michael reaction, the Diels-Alder reaction, or the Friedel and Crafts condensation with benzene in the presence of aluminum chloride were unsuccessful and usually resulted in the recovery of unchanged starting material. A Friedel and Crafts condensation with benzoyl chloride was realized under forcing conditions which consisted in heating the components to 140° in the presence of aluminum chloride and zinc chloride. The

chief product of the reaction proved to be 8-benzoylperinaphthenone-7 (III), for an identical orange-yellow substance was obtained by the condensation of the acid chloride of perinaphthenone-8-carboxylic acid (IX, below) with benzene in the presence of aluminum chloride. The reaction mixture from the benzoylation afforded also a second benzoylperinaphthenone which is less soluble and higher melting (304–307°) than the isomer III, and more highly colored (brownish red). The substance resembles 3,8 pyrenequinone<sup>4</sup> in color and melting point (309°) and may be the 3-benzoyl derivative of I.

In the reaction with hydrogen peroxide in aqueous alcohol in the presence of sodium carbonate, perinaphthenone was found to be at-



tacked much less readily than 2-methyl-1,4-naphthoquinone,<sup>5</sup> but after somewhat prolonged heating the substance was converted into the oxide IV. The isomerization of this substance was effected, as in the naphthoquinone series,<sup>5b</sup> by dissolving the oxide in concentrated sulfuric

(1) (a) Fieser and Hershberg, *THIS JOURNAL*, **60**, 1658 (1938); (b) Fieser and Hershberg, *ibid.*, **62**, 49 (1940); (c) Fieser and Novello, *ibid.*, **62**, 1855 (1940); (d) Fieser and Gates, *ibid.*, **62**, 2335 (1940).

(2) I. G. Farbenindustrie, German Patent 614,940 (1935) [*C. A.*, **29**, 8009 (1935)].

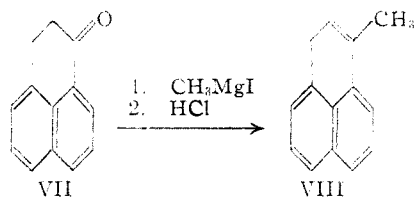
(3) Zil'berman and Barkov, *J. Gen. Chem., U. S. S. R.*, **7**, 1738 (1937) [*C. A.*, **32**, 538 (1938)].

(4) Vollman, Becker, Corell and Streeck, *Ann.*, **531**, 1 (1937).

(5) (a) Fieser, Campbell, Fry and Gates, *THIS JOURNAL*, **61**, 321 (1939); (b) Fieser, *J. Biol. Chem.*, **123**, 391 (1940).

acid and pouring the solution onto ice. This afforded a red, alkali-soluble substance melting at 185° which was characterized by the preparation of yellow acetyl and benzoyl derivatives. The rupture of the oxido linkage must yield either the 7,8- or 7,9-diketo derivative of perinaphthene, or the respective enolic form of one of these substances. Since the 7,9-dione is known<sup>6</sup> and differs in properties from the present substance, the latter must be perinaphthanedione-7,8 or the enol 8-hydroxyperinaphthenone-7 (V). A bromo derivative of presumably corresponding structure (VI) was obtained readily according to a procedure described in the patent literature,<sup>7</sup> but attempts to convert this into the hydroxy compound V were unsuccessful, the substance being recovered unchanged after treatment with silver acetate under forcing conditions.

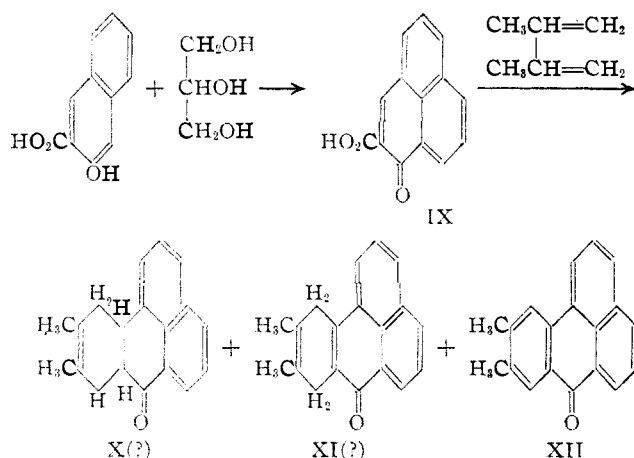
The unsaturated hydrocarbon perinaphthene is unknown, and an attempt in this Laboratory to dehydrate perinaphthanol-7 with potassium bisulfite was unsuccessful.<sup>1a</sup> In the present work, attempts to apply the Tschugaeff reaction, or to effect dehydration through the chloride, were also without positive outcome. A homolog, however, was prepared without difficulty by the addition of methylmagnesium iodide to perinaphthone-7<sup>1d</sup> (VII) and dehydration of the resulting crystalline carbinol with ethanol containing hydrogen chloride. 7-Methylperinaphthene-7 (VIII) was obtained as an initially colorless product melting at 59.5–60.3°, but on exposure to air and light it rapidly darkened and decomposed. Craig, Jacobs and Lavin<sup>8</sup> have de-



scribed a very similar and possibly identical hydrocarbon melting at 63–65° which they isolated as one product of the reaction mixture resulting from the action of methylmagnesium iodide on perinaphthene. The absorption spectrum of our hydrocarbon in ethanol, kindly determined by Dr. R. N. Jones, agrees very closely with that re-

ported by Craig, Jacobs and Lavin except for a slight indication of fine structure in the region of longer wave length.

On finding that perinaphthene remains unchanged after being heated at 100° for two days with 2,3-dimethylbutadiene in a variety of solvents, and that the reaction mixture yields only tars at 200°, we decided to determine if a substituent carboxyl group would lend adequate reactivity to the double bond. 7-Perinaphthene-8-carboxylic acid (IX) was obtained in 18.7% yield according to a patent specification<sup>2</sup> by condensing 2-hydroxy-3-naphthoic acid with glycerol in the presence of sulfuric acid and sodium nitrobenzene sulfonate. It forms golden blades melting at 285°, yields perinaphthene on decar-



boxylation, and gives a crystalline acid chloride. The unsaturated keto acid reacts readily with 2,3-dimethylbutadiene in acetic acid solution at the reflux temperature, and under the mildest conditions of reaction the expected angular carboxyl group is eliminated in the course of the addition. A reaction period of three hours afforded a mixture consisting chiefly of dihydrodimethylbenzanthrone of the possible structure XI, and another substance isolated in small amounts had the composition of a tetrahydride, which may correspond to X. Prolonged refluxing of the acetic acid solution of the components gave a mixture of the dihydride XI and the fully aromatized 2,3-dimethyl-1,9-benzanthrone-10 (XII). The structure of the latter substance was established by oxidation to a hitherto undescribed dimethylantraquinone carboxylic acid, and decarboxylation to the known 2,3-dimethylantraquinone. The dihydro compound can be converted to the benzanthrone XII

(6) Errera, *Gazz. chim. ital.*, **41**, 190 (1911); Fleischer and Retze, *Ber.*, **55**, 3280 (1922); Wojac, *ibid.*, **71**, 1102 (1938).

(7) General Aniline Works, U. S. Patent 2,145,051 (1939).

(8) Craig, Jacobs and Lavin, *J. Biol. Chem.*, **139**, 277 (1941).

by dehydrogenation over palladium charcoal and, indeed, when it is crystallized repeatedly from acetic acid it affords this substance, apparently by a process of disproportionation.

### Experimental<sup>9</sup>

Several lots of perinaphthenone were prepared by the procedure of Fieser and Hershberg<sup>1a</sup> with duplication of the yield reported. It was observed that the compound gives a red vat when treated with sodium hydrosulfite in aqueous-alcoholic alkali.

**Perinaphthenone oxime** was prepared by refluxing the ketone for four hours with a solution of hydroxylamine hydrochloride in absolute ethanol. The purified oxime crystallized from dilute alcohol in yellow blades; m. p. 166.8–167.3°, with sintering at 165°.

*Anal.* Calcd. for  $C_{13}H_9ON$ : C, 79.98; H, 4.65. Found: C, 80.14, 80.24; H, 4.51, 4.74.

**Perinaphthenone—Aniline Bisulfite.**—A solution of 1 g. of perinaphthenone in 95% alcohol was treated with excess saturated sodium bisulfite solution and heated for about fifteen minutes, when the initial yellow color had faded to a weak straw-yellow. Aniline (6 cc.) was added and heating continued for a few minutes, and on cooling in ice the aniline salt of the bisulfite addition product separated as nearly white crystals; yield 1.73 g. (87%). Recrystallization from water gave colorless needles; m. p. 173.2–174.6°, dec.

*Anal.* Calcd. for  $C_{13}H_{11}O_4NS$ : C, 64.21; H, 4.82. Found: C, 63.80; H, 5.00.

When an aqueous solution of the salt is acidified with hydrochloric acid and boiled for a few minutes a yellow precipitate of the original ketone (mixed m. p.) suddenly separates.

**Perinaphthanol** was obtained most satisfactorily by the previously described method<sup>1a</sup> when a two-year old lot of Raney nickel catalyst was used; direct crystallization of the oily reaction product from ligroin gave an 80% yield of the saturated alcohol in the form of light brown prisms; m. p. 83–88°. When freshly prepared and more active catalyst was employed, the reaction mixture contained a considerable amount of phenolic material. On attempted dehydration of the alcohol by the Tschugaeff method, the only product isolated was unchanged starting material which, when purified, formed colorless prisms melting at 99–100.7° (Found: C, 84.83; H, 6.86). Treatment of the alcohol with phosphorus pentachloride and oxychloride, followed by heating with pyridine, gave no clean product.

**7-Methylperinaphthanol-7** was prepared by adding a solution of 5 g. of perinaphthanone-7<sup>1d</sup> in 100 cc. of ether to the Grignard reagent from 0.75 g. of magnesium and 5 g. of methyl iodide. Hydrolysis was effected by adding 5.5 cc. of saturated ammonium chloride solution; after standing for several hours, the clear ethereal solution was decanted from the paste of salts and evaporated. The residual oil crystallized on treatment with petroleum ether and afforded 3.65 g. (67%) of the carbinol; m. p. 68–69.5°. Recrystallization from petroleum ether (20–40°) gave colorless prisms; m. p. 74.6–76.1°.

(9) The melting points are corrected unless otherwise stated.

*Anal.* Calcd. for  $C_{14}H_{14}O$ : C, 84.81; H, 7.12. Found: C, 84.60; H, 7.12.

**7-Methylperinaphthene-7 (VIII).**—Five cc. of absolute ethanol saturated at room temperature with hydrogen chloride was diluted with 10 cc. of absolute ethanol and 1.45 g. of 7-methylperinaphthanol-7 was added. The solution was boiled for fifteen minutes, the solvent removed under vacuum, and the grayish crystalline residue was taken up in petroleum ether (20–40°). The solution was dried and passed through a tower of alumina, and on evaporation of the filtrate there was obtained 1.1 g. (83%) of white plates of the hydrocarbon; m. p. 59.5–60.3°. When the pure material was bottled under nitrogen it turned light green in a few days but showed no sign of further decomposition after several months. Impure samples decompose rapidly in the atmosphere of the laboratory and soon give black tars.

*Anal.* Calcd. for  $C_{14}H_{12}$ : C, 93.29; H, 6.71. Found: C, 92.98; H, 6.77.

The picrate was obtained by adding a cold saturated solution of picric acid in alcohol to a solution of the hydrocarbon in the same solvent. Small, brick red needles separated; m. p. 174.5°, dec. The picrate decomposed on attempted recrystallization.

**Benzoylation of Perinaphthenone.**—A mixture of 10 g. of perinaphthenone, 2 g. of zinc chloride, 50 g. of powdered aluminum chloride, and 25 cc. of benzoyl chloride was stirred mechanically for twenty-one hours in a metal bath maintained at 130–140°. The cooled mixture was decomposed with ice and hydrochloric acid and the product was digested with dilute acid and collected in the form of black, granular material. This was extracted with four 200-cc. portions of boiling benzene and the solution was clarified with Norit, washed with dilute alkali to remove benzoic acid, dried, concentrated, and diluted with hexane. On cooling, **8-benzoylperinaphthenone-7 (III)** separated in the form of clusters of orange plates; m. p. 164–165.5°; yield 5.9 g. (38%). A second crop of less pure material amounted to 1.6 g. The main product on recrystallization from benzene formed yellow blades; m. p. 167.9–168.4°. The substance gives a red vat with alcoholic alkali and hydrosulfite.

*Anal.* Calcd. for  $C_{20}H_{12}O_2$ : C, 84.49; H, 4.26. Found: C, 84.64; H, 4.39.

An isomeric **benzoylperinaphthenone-7** was isolated from the residue from the benzene extraction. The dark solid was extracted with alcohol in a Soxhlet apparatus and afforded 1.53 g. of dark red microcrystalline material. Crystallization from chlorobenzene gave a mixture of slender, brick red needles and small, dark red prisms from which the needles could be separated by flotation and hand picking. There was isolated in all 25 mg. of brownish red needles; m. p. 304–307°.

*Anal.* Calcd. for  $C_{20}H_{12}O_2$ : C, 84.49; H, 4.26. Found: C, 84.64; H, 4.50.

The prismatic material after two recrystallizations melted at 274–275°, dec., and a mixture with the above product began to melt at 267° (Found: C, 83.47, 83.77; H, 3.78, 3.50).

**8,9-Oxidoperinaphthenone-7 (IV).**—A warm solution of 1 g. of perinaphthenone in 10 cc. of alcohol was treated

with a solution of 1 cc. of 30% hydrogen peroxide and 0.2 g. of sodium carbonate in 5 cc. of water. The solution was warmed sufficiently to prevent crystallization (50°) for twenty minutes, during which time gas was evolved and the solution turned dark red. On cooling, the solution deposited 0.63 g. (58%) of crude oxide, m. p. 111–120°, and dilution of the mother liquor with water gave 0.32 g. of crude perinaphthenone, m. p. 130–136°. On acidification of the alkaline liquor, 0.09 g. of crude naphthalic acid was precipitated. The oxide when recrystallized several times from alcohol formed small yellow needles; m. p. 117–117.4°, with sintering at 116°.

*Anal.* Calcd. for  $C_{13}H_8O_2$ : C, 79.58; H, 4.11. Found: C, 79.47; H, 4.33.

**8-Hydroxyperinaphthenone-7** or **Perinaphthanedione-7,8** (V).—The crude oxide (0.67 g.) was stirred with concentrated sulfuric acid (10 cc.) until a homogeneous, deep red solution was obtained. This was cooled in ice and diluted with ice and water until the rearrangement product precipitated. The product when washed and dried consisted of 0.66 g. (98.5%) of an orange powder; m. p. 163–178°. Several crystallizations from dilute methanol gave clusters of light red needles; m. p. 184.4–185°.

*Anal.* Calcd. for  $C_{13}H_8O_2$ : C, 79.58; H, 4.11. Found: C, 79.71; H, 4.45.

The **acetate** formed yellow elongated prisms from dilute acetic acid and melted at 183.5–185.5°.

*Anal.* Calcd. for  $C_{13}H_{10}O_3$ : C, 75.62; H, 4.23. Found: C, 75.62; H, 4.41.

The **benzoate**, prepared by the Schotten-Baumann procedure, crystallized from ethanol in small yellow blades; m. p. 163.5–165.6°, with sintering at 159°.

*Anal.* Calcd. for  $C_{20}H_{12}O_3$ : C, 79.99; H, 4.03. Found: C, 80.01; H, 4.17.

For the preparation of 8-hydroxyperinaphthenone-7 in quantity it was found convenient to treat the crude, moist oxide from 5 g. of perinaphthenone directly with sulfuric acid (25 cc.), pour the solution onto ice, and extract with three 200-cc. portions of benzene. The product was then extracted from the benzene solution with three 200-cc. portions of 5% sodium hydroxide; the red alkaline solution on acidification yielded 2.33 g. of orange hydroxyperinaphthenone, m. p. 178–180°, uncorr.; the yield based upon material consumed is 78%.

**8-Bromoperinaphthenone-7** (VI) was prepared as described in the patent literature<sup>7</sup> by adding 12.5 g. of bromine to a solution of 9 g. of perinaphthenone in 90 cc. of glacial acetic acid and heating the mixture on the steam-bath for one hour; an orange solid separated and gradually turned red. This was collected and washed with acetic acid and then suspended in water and heated for fifteen minutes, when the solid turned yellow. The collected product (12.6 g.) when crystallized from alcohol gave 8.6 g. of yellow needles, m. p. 148–150°, uncorr., and on further purification the substance formed fine yellow needles, m. p. 152–152.4°.

*Anal.* Calcd. for  $C_{13}H_7OBr$ : C, 60.26; H, 2.72. Found: C, 60.06; H, 2.71.

The bromo compound was recovered unchanged after being heated with silver acetate in acetic acid for one week

at the reflux temperature (quantitative recovery) or for forty-five hours at 200° (42% recovery).

**7-Perinaphthenone-8-carboxylic Acid** (IX).—After much experimentation the following version of the patent process<sup>2</sup> was adopted as the most satisfactory found. A 3-liter flask provided with a mechanical stirrer and thermometer was charged with 160 cc. of water, 225 cc. of concentrated sulfuric acid, 90 g. of technical sodium nitrobenzene sulfonate, 140 cc. of glycerol, and 90 g. of 2-hydroxy-3-naphthoic acid, and the mixture was stirred and heated continuously with a free flame at 130–140° for one hour. The tarry, black solution was poured while hot onto 1 l. of ice, diluted to 3 l. and allowed to cool. The supernatant liquor was decanted and discarded and the black residues from two runs were combined and extracted with two 1-liter portions of boiling alcohol, the extracts containing tar and unchanged starting material being likewise discarded. The resulting residue when dried consisted in an olive green powder, and this was then extracted in a Soxhlet apparatus with boiling chlorobenzene. The red solution when concentrated and cooled yielded 60 g. of reddish brown powder, which could be purified by crystallization from either chlorobenzene or acetic acid, with the liberal use of Norit, to give 40 g. (18.7%) of satisfactory material. The purified substance crystallizes from acetic acid in glistening, golden yellow blades which sinter at 275° and melt at 284.4–285° with evolution of gas.

*Anal.* Calcd. for  $C_{14}H_8O_5$ : C, 75.00; H, 3.60. Found: C, 75.15, 74.89, 75.20; H, 3.85, 3.75, 3.86.

Decarboxylation of the acid was accomplished by heating it at 3–5 mm. pressure; the solid distillate obtained when crystallized from benzene melted at 152.7–153.5° and did not depress the melting point of perinaphthenone.

The **acid chloride** was prepared by refluxing for thirty to forty-five minutes a suspension of 2 g. of the acid in 80 cc. of benzene with 3.1 g. of phosphorus pentachloride. The resulting solution on cooling deposited 1.4 g. (65%) of dull orange plates; m. p. 203–210°. Recrystallization from benzene gave microscopic orange blades; m. p. 209–211° (sintering at 207°).

*Anal.* Calcd. for  $C_{14}H_7O_2Cl$ : C, 69.29; H, 2.91. Found: C, 69.38, 69.12; H, 3.12, 3.19.

**8-Benzoylperinaphthenone-7** was obtained by refluxing 1 g. of the acid chloride for three hours with 6 g. of aluminum chloride and 50 cc. of benzene. Acid hydrolysis of the mixture gave an oily product which when fully purified by crystallization from acetic acid formed small yellow needles, m. p. 167.8–168.2° (0.47 g., 40%); this gave no depression when mixed with the sample described above.

*Anal.* Calcd. for  $C_{20}H_{12}O_2$ : C, 84.49; H, 4.25. Found: C, 84.61; H, 4.40.

**Condensation of 7-Perinaphthenone-8-carboxylic Acid with 2,3-Dimethylbutadiene.** (a) **Brief Refluxing.**—In a typical run 2 g. of the acid was refluxed for three hours with 10 cc. of the diene in 60 cc. of acetic acid. Dilution with water and cooling afforded 0.73 g. of microscopic needles, m. p. 140–170°, and the second and third crops combined amounted to 0.48 g. of dark material melting below 100°. Several recrystallizations of the first crop from ethyl acetate, in which the substance is readily solu-

ble, gave fine yellow needles of **6,7-dimethyl-5,8(?)-dihydro-1,9-benzanthrone-10 (XI)**, m. p. 188.6–189.4°. Repeated recrystallization of the dihydride from acetic acid seemed to result in an oxidation and disproportionation with the formation of the benzanthrone XII.

*Anal.* Calcd. for  $C_{19}H_{16}O$ : C, 87.66; H, 6.20. Found: C, 87.62; H, 6.28.

Recrystallization of the combined second and third crops from acetic acid yielded a mixture of orange-yellow needles of the dihydride XI, m. p. 180–184°, and white blades (0.1 g., m. p. 122–123°) of **6,7-dimethyl-5,8,11,12(?)-tetrahydro-1,9-benzanthrone-10 (X)**, which could be separated by hand. Several recrystallizations of the latter substance from dilute acetic acid yielded 50 mg. of small, white needles; m. p. 124.7–125.2°.

*Anal.* Calcd. for  $C_{19}H_{18}O$ : C, 87.32; H, 6.94. Found: C, 87.25; H, 7.02.

(b) **Prolonged Refluxing.**—A mixture of 1 g. of 7-perinaphthenone-8-carboxylic acid and 5 cc. of dimethylbutadiene in acetic acid was refluxed for twenty-four hours, concentrated and cooled, when a crop of orange blades separated consisting largely of **6,7-dimethyl-1,9-benzanthrone-10 (XII)**, as indicated by the fact that but little of the crystallizate dissolved when treated with boiling ethyl acetate. The dihydride XI, which is the chief product when the refluxing is continued for only a brief period, closely resembles the fully aromatic compound in appearance and melting point but is distinguished from this substance in being readily soluble in hot ethyl acetate. The material unextracted by this solvent crystallized from acetic acid in fine orange blades; m. p. 188.6–189.4°. A mixture of a sample with the dihydride XI showed a depression of about 10°.

*Anal.* Calcd. for  $C_{19}H_{14}O$ : C, 88.34; H, 5.46. Found: C, 88.32; H, 5.64.

**6,7-Dimethyl-1,9-benzanthrone-10** also was obtained by heating 0.4 g. of the dihydride XI with 50 mg. of 10% palladium charcoal at 300° until the evolution of hydrogen ceased. Extraction with acetic acid gave 0.2 g. of plates, m. p. 178–184°, and the recrystallized material melted at 189–190° and gave no depression when mixed with the above sample.

**2,3-Dimethylanthraquinone-5-carboxylic Acid.**—A solution of 1.07 g. of crude dimethylbenzanthrone in 20 cc. of acetic acid was treated slowly at 70° with a solution of 4 g. of chromic anhydride in 22 cc. of 90% acetic acid, shaken

at 70° for fifteen minutes and poured into water. On crystallization of the brown precipitate (0.65 g.) from acetic anhydride there was isolated a complex which formed cream-colored blades melting with the loss of solvent at 215–127° and remelting at 312–316°, uncorr. (Found: C, 70.93, 70.96; H, 4.45, 4.47). A solution of the purified complex in hot, dilute ammonia when boiled to expel excess ammonia and acidified with hydrochloric acid gave a pale yellow precipitate of the free acid. The substance darkens at about 310° and melts with decomposition at 313–314°, uncorr. No satisfactory solvent was found for crystallization.

*Anal.* Calcd. for  $C_{17}H_{12}O_4$ : C, 72.85; H, 4.32. Found: C, 72.43, 72.55; H, 4.43, 4.52.

A 0.1-g. sample of the acid was decarboxylated with copper bronze in quinoline at 170° and the residue remaining after extraction and leaching with hydrochloric acid gave, on crystallization from acetic acid, 60 mg. of pale yellow needles of **2,3-dimethylanthraquinone**, m. p. 210.6–211.5°; a mixture with an authentic sample melted at 210–211.7°.

### Summary

Perinaphthenone has been further characterized by the preparation of an oxime, a bisulfite addition product, an oxide, and a bromide. The oxide is convertible in good yield into 8-hydroxyperinaphthenone-7. Benzoylation of perinaphthenone under forcing conditions gives the 8-benzoyl derivative as the chief product, along with an unidentified isomer. 7-Methylperinaphthene-7 was prepared from perinaphthanone-7 by Grignard methylation and dehydration.

While perinaphthenone was found unsatisfactory as a component in the Diels–Alder reaction, its 8-carboxy derivative adds 2,3-dimethylbutadiene readily and affords a new route for the synthesis of benzanthrone. The carboxyl group is lost in the process and the reaction mixtures contain hydro derivatives of 2,3-dimethyl-1,9-benzanthrone-10.

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